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LEACHING OF SOME CHEMICAL CONSTITUENTS FROM COLUMNS WITH RENDZINA SOIL

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Experimental investigation of leaching in which a rendzina material and limestone were treated with plant extracts and chemical solutions has been performed in glass cylinders exposed to a slow flow of different liquids. In general, all elements were more easily leached from the A_1 soil horizon than from the others, what may indicate the influence of complexing by organic matter. The leaching of calcareous soil and parent material simulated, in the laboratory has dissolved the chemical constituents in the proportion indicated the processes of allitization.

Many explanations of soil-forming processes postulate that chemical alteration of rocks and minerals is one of the principal factors which determine the nutrient supply to plants.

The phenomena of alteration may be studied in various ways, one of which may be the simulation of leaching processes in the laboratory. In this experiment the soil columns which where used to study the solubility of trace elements [7] where also utilized for the purpose of investigating some of soil-forming processes. The solvents used in this experiments were similar to those occuring naturaly in soils (with the exception of acetic acid and ammonium oxalate solutions) and should result therefore in reactions which closely resemble the natural field conditions.

MATERIALS AND METHODS

The investigated soil was a well developed, brown rendzina, arable, freely drained and of a heavy loam texture derived from Cretaceous limestone. This was located on a small elevation (about 120 m) near

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Łysaków, voivodeship Kielce, where the mean annual temperature is 7.5°C, and the mean annual precipitation ammounts to 630 mm. The main properties of the soils are given in Table 1.

TABLE 1. SOME PROPERTIES OF THE SOIL USED FOR THE EXPERIMENT

Horizon	Depth of horizon cm	Clay $< 2\mu$ %	pH in 1n KCl	Organic matter %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	CaO %
A_1 — grey heavy loam with small gravel	0—15	39.0	6.3	3.65	70.85	8.11	2.70	0.33	2.31
$A_1/(B)$ — yellowish grey heavy loam with small limestones	15—20	58.0	6.4	2.82	70.20	9.35	2.92	0.69	2.41
(B) — yellowish brown heavy loam with limestones	20—30	55.6	6.2	1.73	66.20	12.31	3.86	0.09	2.00
(B)/C — desintegrated rock with brown clay	30—50	50.3	6.2	1.73	62.83	12.26	3.96	0.27	3.92
C — cretaceous limestone	> 50	—	7.0	—	36.99	5.22	1.40	0.06	28.38

The $< 2\ \mu$ fraction was separated by sedimentation from the water dispersed soil material at pH of 9, which was kept constant with NH_4OH. The clay was floculated with HCl. The air dried clay was then analyzed by a X-ray diffraction in powder form, using Rigaku-Denki diffractometer with Ni-filtered Cu Kα radiation. Some clay samples were examined after Mg^{2+} and glicol saturation and heating. The X-ray examination was made on clay fraction which was separated from natural soil samples and from those taken from the leached soil columns after the completion of the experiment.

The experiment which has lasted for three months is described in details elsewhere [7]. The soil columns were exposed to a slow flow of the following liquids:

I. Aqueous extract of oak leaves, pH 4.8
II. Aqueous extract of pine needles, pH 4.4
III. Aqueous extract of lupine, pH 5.1

IV. Ammonium oxalate solution, 0.2 M, pH 3.2
V. Water saturated with CO_2, pH 4.0
VI. Acetic acid, 2.5%, pH 2.5

RESULTS AND DISCUSSION

The clay fraction of the investigated soil consists of the montmorillonite mineral group and of mixed layer minerals. The investigation also revealed a considerable amount of quartz together with cristoballite present in this fraction. Hydromicas and kaolinite occur in negligible quantities. The predomination of montmorillonite in soil highly influences all its properties. Minerals of this group are known to be capable of fixing several cations and of forming clay-organic matter complexes [8, 10].

Within a relatively short time of the investigation (3 months) it has been shown, that when leaching a calcareous soil material with different extractants, it can result in the dissolution and translocation of several chemical elements and the development of profiles with defined zones.

The extend of the differentiation within the soil columns varied according to the kind of percolating liquids. In the columns treated by plant extracts three zones were observed from the top: dark brown, greyish brown and grey with characteristic gleying and mottling air pipes. Acetic acid and ammonium oxalate solutions resulted in formation of deep colour-less zones in soil cores.

The experiment conducted with the parent limestone has also produced some changes in the rock particles. In all columns leached with the aqueous extracts of plant material, the rock pieces became coated with a brown organic compoud. The limestone which was subsequently extracted with an ammonium oxalate solution and acetic acid has slightly disintegrated and became lighter in colour. Only the limestone which was treated with CO_2-water remained unchanged.

It is known, from the studies of Atkinson and Wright [1] and of Bloomfield [2] that aqueous extracts of tree leaves are more active in the dissolution of some cations than are the grass extracts. Polyphenols appear to be mainly responsible for these properties of the leaf extract. Davies *et al.* [5] showed that polyphenols can reduce ferric compounds and form a no-ionic complex capable of moving freely in soil solution without ionic exchange.

Some reactions of the extractants with soil material can be expected. Decomposition of several soil minerals under the influence of percolating liquids is well known [3, 4, 9]. The formation of clay-organic matter complexes may also occur [10]. In order to observe the changes in clay minerals under the conditions of a leaching experiment the clay fraction was separated from the bisected soil cores and was then examined under the diffractometer. The smoothed tracings of X-ray diffraction patterns of this fraction from the bottom part of soil columns are presented in Figure 1. The most notable changes for the A_1 horizon occurred at the range from 14 to 20 Å. The examined clay fractions taken from the upper parts of soil columns show similar but smaller changes in the montmorillonite mineral group. The most distinct decreases in the reflections from 10 to 18 Å, are observed in clay separated from the soil material of the (B) horizon which was leached with the ammonium oxalate and acetic acid solutions. The water extract of lupine caused the greatest changes in the d_{001} spacing of montmorillonite, shifting the low broad peak at about 12 Å toward 20Å. Similar changes are observed for the clay saturated with magnesium (Fig. 1). Schnitzer and Kodama [10] repoted also that interaction of the montmorillonite with fulvic acid increased the d_{001} spacing. That may indicate the formation of a natural clay-organic matter complexes.

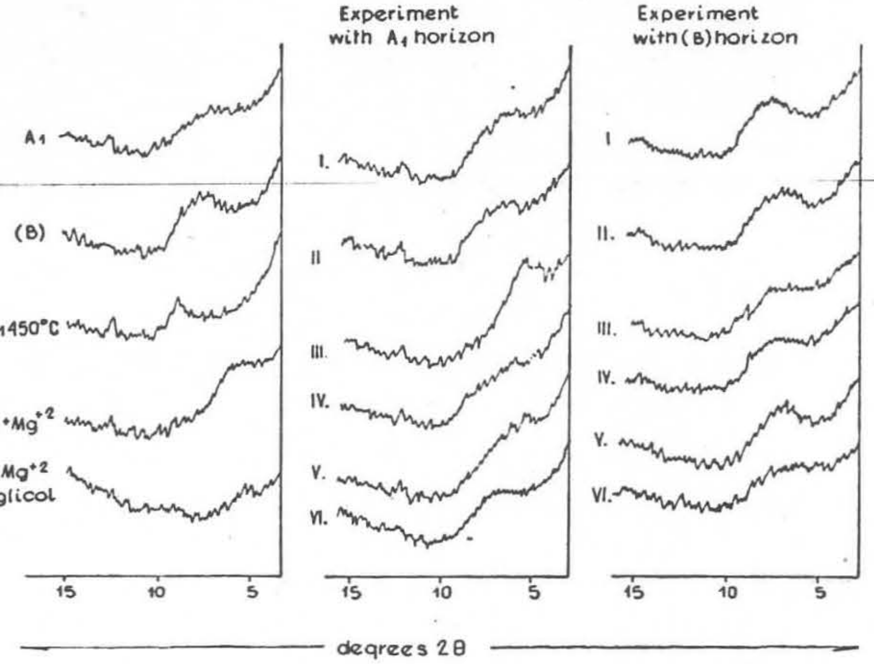

Fig. 1. Changes of X-ray diffraction patterns of the clay fraction under different treatment and leaching with extractans

aqueous extracts of: (I) oak leaves, (II) pine needles, (III) lupine; and aqueous solutions of: (IV) ammonium oxalate, (V) carbon dioxide, (VI) acetic acid

Although clay minerals are liable to be decomposed by acid it was found, in this experiment, that all investigated extractants dissolved only a very small amount of silica from soil so that decomposition of mineral was not serious (Tab. 2). However, Carror and Starkey [3] reported that CO_2-water dissolves silica, mainly from montmorillonite in a limestone environment. The mobilization of aluminium was also negligible with the exception of the A_1 horizon from which 11 per cent of total aluminium content was exctracted with ammonium oxalate solution (Tab. 2). A high solubility of this element (up to 10 per cent of the total content) was also found by Gad and Le Rich [6]. It seems most unlikely that much of this aluminium resulted from the breakdown of clay minerals, but it is rather possible that this aluminium was complexed by organic matter.

The development of defined zones within each of the soil columns could suggest that the changes in colour are connected with the reduction and movement of ferric compounds. The distribution of iron in the soil columns after the leaching indicates that a very limited degree of iron translocation has occurred within the soil cores. The only exception was under the treatment by an oxalate solution, which had resulted in a considerable amount of iron which was leached and transported downward in both of the soil horizons. It appears therefore that the grey colour associated with the gleish zones results from the removal of ferric oxide coatings. However the soil material retains a large pro-

TABLE 2. THE LEACHING OF CHEMICAL CONSTITUENTS FROM SOIL MATERIAL (IN mg/g)

Extractant	Soil horizon	Si	Al	Fe	Mg	Ca	Na	K
I	A_1	8.75	0.94	1.78	22.29	71.48	3.77	2.68
	(B)	9.14	0.68	2.17	8.42	27.82	1.44	1.81
	C	10.95	0.45	0.27	15.26	46.06	1.83	0.32
II	A_1	12.50	1.12	7.85	30.64	114.35	6.25	2.63
	(B)	8.27	0.61	2.72	9.90	29.89	1.98	4.71
	C	10.60	0.79	0.36	23.98	35.68	1.51	0.55
III	A_1	8.75	1.83	3.93	57.93	125.35	7.53	2.50
	(B)	7.43	1.35	0.98	24.64	111.32	3.86	4.10
	C	10.63	0.39	0.28	34.61	61.11	10.56	27.27
IV	A_1	20.00	231.19	38.54	29.81	67.45	6.24	46.25
	(B)	9.00	22.00	16.64	17.55	39.37	5.25	19.04
	C	22.04	1.03	0.45	21.31	6.01	5.78	7.45
V	A_1	33.75	5.85	3.61	54.31	184.24	7.63	10.00
	(B)	56.43	3.83	4.13	19.41	82.24	6.17	6.74
	C	10.76	0.54	0.26	13.12	31.82	3.28	0.53
VI	A_1	215.00	27.36	3.28	98.93	655.84	22.50	23.75
	(B)	198.00	10.87	4.14	57.34	218.49	12.19	22.90
	C	53.70	0.19	0.80	210.19	5409.68	108.60	4.87

portion of the original content of iron. Bloomfiel [2] and Siuta with Motowicka-Terelak [11] have had offered similar explanations of the phenomena which they observed in their experiments.

The solubility of chemical constituents as calculated on the basis of their percentage solubility are as follows:

A_1 horizon: $Mg > Ca > Na > Al > K > Fe > Si$
(B) horizon: $Mg > Ca > Na > K > Fe > Al > Si$
C horizon: $Mg > Na > Ca > K > Fe > Si > Al$

Field and laboratory evidences show that under certain conditions iron can be readely mobilized and transported within a soil profile and that some ferric compound seems to be one of the relatively less soluble of the common chemical constituents.

The ratios of SiO_2/Al_2O_3, calculated for dissolved elements, increases remarkably from the upper soil horizon toward the limestone. Although this trend is notable for all kind of extractants. The ratio was extremely variable for the ammonium oxalate solution, from 0.02 to 44.00. The ratios of SiO_2/R_2O_3 indicate that the most soluble forms of iron were present in the A_1 horizon and that the mobility of iron in the limestone was negligible.

Decomposition of the silicate framework in this experiment was negligible even under the treatment by such active agents as ammonium oxalate and acetic acid solutions. The changes observed in the clay minerals were related rather to the formation of montmorillonite-organic matter complexes.

The activity of both, the plant extracts and the chemical solvents, was quite high in dissolution of carbonates in limestone.

The colour changes observed in the soil columns were due to the reduction of ferric compounds rather than to their movement. Only ammonium oxalate solution has produced a considerable downward translocation of iron in the soil columns.

The leaching of the calcareous soil and parent material in the soil columns, has dissolved the chemical constituents in the proportions indicated according to Pedro [9] the processes of allitization.

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ŁUGOWANIE NIEKTÓRYCH GŁÓWNYCH SKŁADNIKÓW CHEMICZNYCH Z RĘDZINY UMIESZCZONEJ W CYLINDRACH

Przeprowadzono doświadczenie w zakresie ługowania rędziny i jej skały macierzystej w cylindrach, poddanych powolnemu przepływowi różnych roztworów.

Na ogół wszystkie składniki chemiczne były łatwiej ługowane z poziomu A_1 niż z innych poziomów glebowych. Łatwo rozpuszczalne związki tych pierwiastków występują w poziomie A_1 przypuszczalnie w wyniku kompleksowych połączeń z substancją organiczną.

Ługowanie rędziny różnymi roztworami w warunkach doświadczenia laboratoryjnego powodowało uruchamianie głównych składników chemicznych w proporcjach wskazujących na procesy typu alicznego.

Translator: The Author